Bio-based phenols and fuel production from catalytic microwave pyrolysis of lignin by activated carbons

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HIGHLIGHTS

- Catalytic microwave pyrolysis of lignin from activated carbon was investigated.
- 45% of phenol, 78% of total phenolics, and 15.3% of hydrocarbons were achieved.
- The heating value of lignin-derived biochars was significantly higher than lignin.
- The thermal degradation and reaction mechanism were analyzed.

ARTICLE INFO

ABSTRACT

The aim of this study is to explore catalytic microwave pyrolysis of lignin for renewable phenols and fuels using activated carbon (AC) as a catalyst. A central composite experimental design (CCD) was used to optimize the reaction condition. The effects of reaction temperature and weight hourly space velocity (WHSV, h^{-1}) on product yields were investigated. GC/MS analysis showed that the main chemical compounds of bio-oils were phenols, guaiacols, hydrocarbons and esters, most of which were ranged from 71% to 87% of the bio-oils depending on different reaction conditions. Bio-oils with high concentrations of phenol (45% in the bio-oil) were obtained. The calorific value analysis revealed that the high heating values (HHV) of the lignin-derived biochars were from 20.4 to 24.5 MJ/kg in comparison with raw lignin (19 MJ/kg). The reaction mechanism of this process was analyzed.

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1. Introduction

The rapid depletion of fossil fuels is leading to the global energy crisis; as a result, the cost of crude oil is increasing eventually. Additionally, the negative side effect led by burning of fossil fuels, such global warming and the formation of acid rain, is becoming one of the biggest challenges in human history. Therefore, considerable researches are focusing on developing alternatives for fossil fuels in the past two decades. As the major feedstock of second generation biofuels, an increasing attention has been paid to converting lignocellulosic biomass into liquid fuels and value-added chemicals.

Lignin is the second abundant component in lignocellulosic biomass following cellulose; it comprises about 23–33 wt.% and 16–25 wt.% of the mass in softwoods and hardwoods, respectively (Mohan et al., 2006), and contributes about 40% of energy content in lignocellulosic biomass (Holladay et al., 2007). Lignin is composed of three phenylpropenyl units: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. From the thermal behavior view of point, lignin is the most heat-resistant component among the major components of lignocellulosic biomass. As a result, more residual char was produced during lignin pyrolysis than pyrolysis of lignocellulosic biomass. Phenols are produced through the cleavage of ether (mainly α or β-o-4 bonds) and C—C linkages during pyrolysis of lignin (Chen et al., 2001; Mohan et al., 2006). Lignin sources are becoming more abundant with the development of lignocelluloses-to-ethanol industry (Pandey and Kim, 2010). Besides, it is well-known that lignin is the main by-product of conventional pulp and paper industry. However, the main use of lignin is as a low-grade energy source in combustion and has not received much attention until recently (Huber et al., 2006). Holladay et al. (2007) evaluated the potential of making use of lignin for value-added chemicals from biorefinery lignin; they pointed out that the overall revenue will be improved from $12 to $35 billion if the lignin is used for purposes, such as chemicals

and transportation fuels, other than low-grade energy source for power. And the market value implies that the products potentially derived from lignin such as phenols (phenol: \$0.55–\$0.65/1b; substituted phenols: \$0.7–\$2.00 1b) are attractive (Holladay et al., 2007).

The characteristics of chemical structure and the abundance of lignin suggest that it has great potential to be used as value-added chemical feedstock such as phenol, benzene, toluene and xylene. Holladay et al. (2007) mentioned that lignin is the only renewable source of the aromatics. Phenolic compounds are workhorses in the chemical industry such as synthesis of phenol formaldehyde resin and plastics (Kleinert and Barth, 2008; Pandey and Kim, 2010). The low molecular weight of products resulted from high degree of depolymerization suggests that pyrolysis may be useful for the controlled molecular weight reduction of lignin (Holladay et al., 2007).

Pyrolysis of biomass is a thermal decomposition process of organic compounds in the absence of oxygen to obtain char, syngas, and bio-oil. Pyrolysis has been widely used for production of liquid fuels and value-added chemicals (Mohan et al., 2006; Bu et al., 2012; Chen et al., 2001). Microwave pyrolysis is a process that transfers heat from the inside to the surface of biomass by microwave irradiation. Comparing with conventional pyrolysis, the advantages of microwave pyrolysis include fast and selective heating, energy efficiency and cost effectiveness (Fernandez et al., 2011; Luque et al., 2012; Hu et al., 2012). Recent studies on microwave pyrolysis of biomass include the conversion of wood (Bu et al., 2012; Salem and Ani, 2012; Wang et al., 2012), sewage sludge (Mendez et al., 2004; Dominguez et al., 2008) and microalgae (Du et al., 2011; Hu et al., 2012).

Recently, a multitude of researches focused on pyrolysis of lignin (Wild et al., 2012; Brebu and Vasile, 2010; Luo et al., 2012). And some attempts aim to displace phenol in the phenol formaldehyde resin synthesis (Xu and Leitch, 2010; Wang et al., 2009; Cheng et al., 2010). However, so far there are only few reported investigations on microwave-assisted pyrolysis of lignin for value-added chemicals and fuels (Chan and Krieger, 1981).

Therefore, the aim of the present study is to make use of lignin as a model compound for renewable phenols and fuel production by catalytic microwave pyrolysis, which will shed light on the reaction pathway of microwave pyrolysis of lignocellulosic biomass and application of lignin. The effects of reaction temperature and weight hourly space velocity (WHSV, h^{-1}) on product yield were investigated and models to predict the product yields were established as well. The chemical compositions of the resulting bio-oils were characterized by GC/MS analysis and the heating value of the bio-char was determined. The reaction mechanism of catalytic lignin pyrolysis was analyzed.

2. Methods

2.1. Materials

The alkali lignin (CAS number 8068-05-1) was purchased from Sigma–Aldrich Corporation (St. Louis, MO, USA). The lignin was used as received. GAC 830 PLUS, an activated carbon (AC) with high purity produced by steam activation of selected grades of coal was purchased from Norit Americas Inc. (Marshall, TX, USA). Sodium ethoxide (Catalog No. AC16859-5000), sodium hydroxide and methyl red indicator (Catalog No. S25435) were purchased from Fisher Scientific Corporation (Pittsburgh, PA, USA).

2.2. Microwave pyrolysis of lignin

Fig. 1 shows the schematic diagram of the microwave-assisted pyrolysis system. The microwave pyrolysis system mainly

consisted of several components: a 1000 W, 2.45 GHz microwave cavity, an infrared temperature sensor for temperature measurement, a 500 mL quartz flask inside the microwave oven which loaded the biomass, and a product cooling and collection system where the condensable liquid (bio-oil) was collected. The temperature of cooling water in condensers was about 5 °C. The microwave reactor was manufactured by Sineo Microwave Chemistry Technology Company (Shanghai, China). A constant microwave power setting (700 W) was used. The reaction temperature of lignin was monitored by an infrared sensor through a closed end quartz tube which was penetrated to the central of the reaction flask. After reaching desired reaction temperatures, the microwave reactor equipped with automatic temperature/power control used a minimum power (e.g., 0–100 W) to maintain the desired reaction temperatures. The system was purged with nitrogen on a flow rate of 1000 mL/min for 15 min prior to pyrolysis reaction to maintain an oxygen-free environment. The weight of syngas product was calculated using the following equation:

$$\text{Weight of syngas} = \text{initial lignin mass} - \text{biooil mass} - \text{biochar mass} \qquad (1)$$

2.3. Experimental design

A central composite experimental design (CCD) was employed to optimize the process conditions and product yields distribution. The reaction temperature (X_1, °C) and weight hourly space velocity, WHSV (X_2, h^{-1}), were selected as independent variables. The weight of lignin feed was 20 g, and activated carbon mass was in the range of 31.8–88.2 g. The product yields of bio-oils, gas, and biochar were chosen as dependent variables. The reaction time was recorded after the desired temperature was reached. For statistical calculations, the variables X_i are coded as x_i according to Eq. (2):

$$x_i = (X_i - X_0/\Delta X) \qquad (2)$$

where X_i is the coded value of an independent variable, X_i is a real value, X_0 is a central value of the independent variable, and $X_0/\Delta X$ is the step change. A 2^2-factorial CCD, with 4 axial points $\left(\alpha = \sqrt{2}\right)$ and 3 replications at the center points leading to a total number of 11 experiments was employed to optimize the reaction conditions. The second degree polynomials (Eq. (3)) were calculated with the SAS statistical package (SAS Institute Inc., USA) to estimate the response of the dependent variables:

$$Y_i = b_0 + b_1 X_1 + b_2 X_2 + b_{11} X_1^2 + b_{21} X_2 X_1 + b_{22} X_2^2 \qquad (3)$$

where Y_i is predicted response, X_1, X_2 are independent variables, and b_0, b_1, b_2, b_{11}, b_{22} and b_{21} are regression coefficients.

2.4. GC/MS analysis of bio-oils

The liquid product was bio crude oil collected after pyrolysis and condensation of volatile products. The chemical composition of bio-oils was determined with an Agilent gas chromatography–mass spectrometer (GC–MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. The GC was programmed to heat to 40 °C for 0.5 min followed by heating to 300 °C at a rate of 10 °C/min. The injection sample size was 1 µL. The flow rate of the carrier gas (helium) was 0.6 mL/min. The ion source temperature was 230 °C for the mass selective detector. Compounds were identified by comparing the spectral data with that in the NIST Mass Spectral library.